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1904

INORGANIC CHEMISTRY AND THE PHASE RULE.*

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As we look back over the history of chemistry, we see always the result of the two opposing forces, one that complicates and one that simplifies. The discovery of new facts makes the science more complex and more difficult to grasp. The discovery of new relations makes the science more simple because it enables us to correlate facts and thus to get a better grasp of the subject. The effect of the generalization in simplifying a single science or in unifying a group of sciences is overlooked by those who complain that the scientific man of the future will be a narrow specialist, knowing only a small part of a single division of one science. While this is always possible, it does not seem probable to me and I think it is much more likely that the chemist of the next generation will be a much better all-round man than any of us can hope to be.

In inorganic chemistry there is one great simplifying generalization with which we are all familiar, the Periodic Law. It has its imperfections and there are some who think that its

*A lecture delivered before the Scientific Faculty and students, University of North Carolina, February 12th, 1904.

shortcomings over-balance its merits. Despite all hostile criticism, the periodic law is today the basis of classification for all advanced work in inorganic chemistry and its influence is marked even in the teaching of elementary chemistry. The periodic law enables us to correlate, more or less well, a large number of facts in regard to the properties of the elements and of their compounds. Yet people were slow in recognizing the full bearing of the statements that "the properties of the elements are a periodic function of their atomic weights" and I do not know what would happen if the law were being advanced today for the first time. There is a mathematical sound about the words "periodic function" which I fear might stamp the law as "too theoretical for the chemist."

While the Periodic Law enables the chemist to predict what the properties of certain substances will be, it concerns itself with these only and has nothing to do with the methods of preparation and separation in use by the chemist. This gap is filled by the second great simplifying generalization, the Phase Rule. So long as we are considering only the cases most studied by the chemist, those involving changes of concentration, pressure and temperature, we may state the phase rule in a relatively simple form: "When passive resistances to change are eliminated, the degrees of freedom of the system are two less than the difference between the number of phases and the number of components." Each chemically and physically distinct mass in the system constitutes a phase. Thus we may have the vapor phase, one or more liquid phases, and one or more solid phases. With ether and water we get two liquid phases; red and yellow phosphorus are two solid phases; so are ice and salt; while sodium sulphate decahydrate is only a single phase.

The statement that "the degrees of freedom are two less than the difference between the number of phases and the number of components" does not sound like a very important one. I can remember the time when I thought that people made a good deal of unnecessary fuss over the phase rule. It

seemed to me an interesting mathematical relation but nothing more. That was ten years ago. Today, I am willing to say that the phase rule offers the rational basis for the classification of phenomena in inorganic chemistry and that it is perhaps the most valuable instrument of research that we possess. In view of the fact that probably ninety-nine per cent of the inorganic chemists make no use of the phase rule, these may seem rather bold statements. I am going to try to justify them. We will consider the phase rule first as a basis of classification and then as an instrument of research.

There are two criteria by which we may judge a method of classification. It must cover the whole ground and the divisions must be rational and not arbitrary. Our first division of the subject is by components. We consider separately systems composed of one, two, three, four or more components. Under each of these divisions we make further sub-heads depending on the number of phases. Thus under one-component systems we should take up first one-phase systems and should discuss the general and specific properties and characteristics of gases, liquids and solids. When considering the specific properties of specific substances, these substances can be taken in an order based on the Periodic Law. In the one-phase one-component systems and in all the other divisions we can arrange our material, in so far as is desirable, according to the Periodic Law. Under two-phase one-component systems, we classify liquid and vapor or boiling-point phenomena, solid and vapor or sublimation phenomena, liquid and solid or freezing-point phenomena, solid and solid or allotropic phenomena. Under three phases we describe such phenomena as the freezing-point of water, the equilibrium between monoclinic sulphur, rhombic sulphur and vapor or melt. Under this same heading comes the general question of monotropic and enantiotropic forms. While chemical action appears to be excluded in one-component systems, such polymerized vapors as acetic acid, sulphur and nitrogen dioxide introduce changes involving the law of definite and multi-

ple proportions, and form an introduction to two-component systems.

Under two-component one-phase systems we have mixtures of indifferent gases, dissociation of gases, mixtures of liquids with and without formation of compounds, solid solutions. With solid and vapor we can have a dissociating solid compound, or a compound existing in the vapor only, such as the oxides of carbon in equilibrium with carbon, or nickel carbonyl. Under solution and vapor we get Henry's law, the law of van't Hoff and Raoult, the phenomena of osmotic pressure, all boiling-point phenoma and the theory of electrolytic dissociation. The other cases of two-phase equilibria involve solubility under pressure. With three phases we have the dissociation pressures of compounds such as hydrated salts, calcium carbonate, etc.; solubility relations, freezing-point determinations, etc.; while with four phases we get the characteristic properties of the quadruple point.

With three components we get more of the characteristic reactions of chemistry. The reaction between carbon monoxide and water belongs under the heading of vapor phase; the formation of esters in organic chemistry is referred to systems involving a liquid phase; the solubility of gases in solutions belongs under two phases, liquid and vapor. With three components and three phases, we get the precipitation of a salt by another salt or by a liquid, the conditions of existence of double salts, the blast-furnace reactions, the reduction of chlorides or sulphides by hydrogen, the facts in regard to shaking out, many of the facts concerning dyeing, fractional crystallization, occlusion, theory of indicators, etc.

With four components we get the solubility changes with two salts having no ion in common, fractional precipitation and also many cases of fractional crystallization. A very large number of chemical reactions involve only four components and therefore come in here.

It will probably seem as though I have laid more stress on physical chemistry than on inorganic chemistry. This is how-

ever more apparent than real. Inorganic chemistry, as a present practiced, consists chiefly in the preparation and study of certain compounds, and to a lesser extent in the study of reactions, usually a qualitative study. In so far as we are dealing with single substances, all that is inorganic chemistry as well as much more finds its place under one-component systems. The preparation of compounds involves phase separation by definition and is therefore included under what is called physical chemistry. The study of reactions is physical chemistry pure and simple. In fact, inorganic chemistry is merely one part of what should be called chemistry, but which unfortunately is called physical chemistry. I quite appreciate that many people take physical chemistry to mean the theory of dilute solutions. That is a very natural mistake which is made even by some who call themselves physical chemists. If one accepts my definition of physical chemistry as the science of chemistry, it is clear that it includes inorganic chemistry and that it includes very much more than the theory of dilute solutions.

I have tried to show that the phase rule offers a satisfactory basis for the classification of practically all the phenomena of inorganic chemistry. For the present, we cannot include much of organic chemistry any more than we can include potassium chlorate, because we are dealing with passive resistances to change in these cases. I look upon this as a temporary limitation and I have hopes that some day it will be possible to present organic chemistry as a system made up of carbon, hydrogen and oxygen as the independently variable components. The recent work of Sabatier and Senderens on the catalytic action of nickel and copper makes the application of the phase rule to organic chemistry a problem of today; but the work has not yet been done and for that reason I have discussed the phase rule only in its bearing on the classification of inorganic chemistry. It is now in order to ask what use the phase rule has been and will be in promoting research.

We will start with an apparently complicated case of solutions containing three or more components. Here the phase rule has brought order out of chaos. It is merely a question of time to determine the conditions of existence for all the possible compounds or solid solutions. The experiments of van't Hoff on the Stassfurt deposits have shown what the composition of the original sea was, why the salts have come down as they have, and even the temperature at which the water was evaporated. His work has furnisned the scientific explanation for the methods of separation worked out empirically at Stassfurt and led to new methods.

There are today many chemists who throw up their hands in despair when they encounter a double salt which cannot be recrystallized without change and yet this is a very simple problem with the phase rule to guide one. The phase rule enables us to tell whether a given solid is a mixture, compound or solid solution. When we reflect on the number of imaginary double salts and basic salts which encumber the literature, we see how sorely such a criterion has been needed in the past. We are now able to attack the problems of fractional crystallization and precipitation in a rational manner.

Today new methods of separating rare earths are coming into use; but, in the past, it has been largely a matter of fractional crystallization and of fractional precipitation. These methods have been slow and not very certain; but how much of that is due to the man and how much to the method? How many of those who have worked with rare earths could take such a relatively simple problem as to separate NaCl and KCl by fractional crystallization, getting the whole of each pure? If one cannot do that, why should one expect to make rapid headway in the separation of an unknown number of unknown substances, which may or may not crystallize together as compounds or solid solutions? Here is a simple instance of the confusion which may easily arise. If one takes a certain solution of copper chloride, potassium chloride and water, cool it to a certain temperature and filter, there

will be left on the filter the red salt $KClCuCl_2$. If the solution is cooled to a slightly lower temperature before filtering, the crystals will be a mixture of the red salt and a green salt $CuCl_2.2KCl.2H_2O$. If the filtration had taken place at a still lower temperature, the precipitate would have been the green salt alone. That is confusing enough but it is not all. If the red salt is washed with water, the green salt is formed while cupric chloride will go into solution. If the green salt is washed with water, a white salt, KCl, is left behind. This is bad enough when the three salts are colored differently; but it is nothing to the difficulties that would beset a man if the salts were all colorless, had the same properties, and could be distinguished chiefly by their unknown atomic weights. This is not mere fancy. I could cite an instance in which two distinguished chemists analyzed what was in all probability a mixture of two salts, believing it to be homogeneous. They were thus led to assume the existence of two new elements, the presence of which could not be shown in any other way.

The whole question of alloys has been put on a rational basis by means of the phase rule. Roozeboom has outlined the methods for studying iron and steel; Heycock and Neville have cleared up the question of the bronzes. We can now distinguish in a way that we never could have done before between states of hysteresis and states of equilibrium. When we eliminate hysteresis, the densities of alloys vary with the composition just as they should. It seems not unreasonable to hope that the tensile strength and other engineering properties of annealed alloys will also vary regularly with the percentage composition. The experience we have gained with salt solutions and with fused alloys will stand us in good stead when we come to consider fused magmas. I feel certain that many of the problems of geology can be solved only by an intelligent application of the phase rule. Recently some people have tried to make certain minerals synthetically by fusing together the components in the proportions in

which they occur in the mineral. This can be successful only in case the chilled melt is annealed thoroughly. Merely allowing the melt to cool will not give the desired result.

Another matter in which the phase rule has been of great value is in analysis in cases where a pure compound cannot be isolated. Under these circumstances, the ordinary methods of gravimetric and volumetric analysis are inapplicable. By methods based on the phase rule, it has been possible to determine with accuracy the composition of compounds crystallizing from a molten mass of metal.

Analyses of efflorescent salts containing water or acid of crystallization are necessarily inaccurate because there is no way of drying the compounds enough to remove all the mother liquor without running the danger of removing some of the volatile component. By the new methods this difficulty no longer exists because the compound can now be analyzed while in the solution.

As yet no one has applied these methods to the analysis of colloidal precipitates, but there seems to be no reason to suppose that this cannot be done. The methods of the phase rule have already been used with success in determining the composition of hydrated beryllium sulphate. The whole question of colloidal precipitates has taken on a new aspect since van Bemmelen began the study of the equilibrium relations with reference to the phase rule.

No matter where one turns, in the whole field of inorganic chemistry, one finds the phase rule useful as an instrument of research. This has come about in the last few years and is but an earnest of what is to be done in the future. When the domain of the phase rule has been extended to cover the whole of organic chemistry and of electrochemistry, every one will then admit the truth of my theses "that the phase rule offers the rational basis for the classification of all chemical phenomena and that it is perhaps the most valuable instrument of research that we possess."

EAST AMERICAN THORNS.*

W. W. ASHE.

TOMENTOSAE.

CRATAEGUS OBESA. A slender narrow crowned tree, seldom exceeding 4 m in height, with nearly black scaly bark on the armed trunk and slender orange or russet pubescent twigs sparingly armed with short 2–3 cm-long thorns. Leaves broadly ovate or nearly orbicular, 7–10 cm long, 5–7 cm wide, rounded or broadly cuneate at base, with many pairs of short ascending notches above the middle, dark green above, paler and tomentose beneath, petioles margined above. Flowers, appearing usually the first week in June in large compound tomentose corymbs, are about 16 mm wide; stamens small, 20. Fruit, borne in large compound clusters, ripening in September and falling after the leaves, is globose or slightly oblong, 8–9 mm thick, scarlet, often capped by the very small narrow reflexed lobes, or the lobes and tube projection deciduous; fleshy pulpy, seed usually 2, hemispherical.

St. Louis County, Missouri. Dr. N. M. Glatfelter. Apparently frequent in eastern Missouri.

TENUIFOLIAE.

CRATAEGUS UBER. A slender tree 3–6 m high with thin gray scaly bark on the trunk, and slender dull chestnut twigs sparingly armed with 3–6 cm-long thorns. Leaves thin, glabrous, ovate or oval, 5–6 cm long, 4–6 cm wide, rounded or narrowed at the broad, often oblique base, several pairs of short acute ascending lobes from near the base; petiole slender, 3–4 cm long. Flowers, appearing about the 20th of May in small loose compound many-flowered pubescent corymbs, are about 20 mm wide; stamens 5–8, usually 5, anthers purple. Fruit, borne in small compound clusters on long slender

* Issued June 15, 1904.

drooping pedicels, ripening late in September and falling with and before the leaves, is oblong, 14–18 mm long, 12–15 mm thick, full and rounded at the ends, dark dull red, mottled with orange at apex, capped by the long narrow brown spreading or ascending lobes which are finely and sharply serrate above the middle; flesh firm, white, juicy and sweet, seed 4–5, 7–8 mm long, narrowed at base, the face narrow.

Summerville, St. Clair Co., Mich. W. W. Ashe, Oct., 1902; C. K. Dodge and W. W. Ashe, Oct. 1903; C. K. Dodge, May, 1903.

CRATAEGUS PERLEVIS. A shrub seldom 3 m high, with ascending branches and purple-brown twigs, armed with numerous 2–5 cm-long thorns. Mature leaves glabrous, pale green, thin but firm, broadly to narrowly ovate, 3–5 cm long, 2.5–5 cm wide, rounded at the broad base, 3 to 4 pairs of short acute lobes, sharply and finely serrate; petiole short but slender. Flowers, appearing the middle of May in glabrous, many-flowered compound corymbs, are about 15 mm wide; stamens 8–10: anthers light red-purple. Fruit, ripening late in September and falling in September and October with and after the leaves, borne in small compound or simple clusters on very slender, rather long pedicels, is pyriform, obovate or rarely oblong, 11–13 mm long, 8–12 mm thick, dark dull red or scarlet, the apex usually much blotched with orange or russet, the narrow entire glabrous lobes short-stalked and appressed.

Berks County, Pennsylvania. Sept., 1901, W. W. Ashe; May and Sept., 1902, May and Sept., 1903, C. L. Gruber; W. W. Ashe, Sept., 1903.

CRATAEGUS OTIOSA. A much branched shrub 3 m in height with a large spreading crown, and slender glabrous, dull red-brown twigs sparingly armed with 2 cm long thorns. Leaves glabrous, rather firm, broadly oval to ovate, the blades 4–6 cm long, 3.5–5 cm wide, truncate to broadly cuneate at base, sharply doubly serrate; many pairs of short broad ascending lobes from near the base; petiole slender, 2–3.5

cm long. Flowers, appearing the last of May in large loose compound many-flowered glabrous clusters, are about 16 mm wide, stamens 5–8. Fruit, borne in loose compound many-fruited pendent clusters, ripening from the first to the middle of October, is oblong, 11–13 mm long, 8–10 mm thick, russet or at length scarlet, the flesh firm, white and juicy; lobes narrow, entire, reflexed or deciduous, seed 3 or 4, small.

Summerville, St. Clair County, Michigan; W. W. Ashe and C. K. Dodge, September, 1902, and October, 1903; C. K. Dodge, May and September, 1903.

CRATAEGUS RETRUSA. A shrubby tree seldom more than 4 m in height with slender chestnut twigs and stout 2–4 cm-long slender ascending thorns. Leaves thin, glabrous, ovate or broadly ovate, 4–6 cm long, 3.5–4.5 cm wide, rounded or broadly cuneate at base, with several pairs of short broad notches, finely doubly serrate. The flowers, appearing about the 20th of May in loose glabrous compound many-flowered clusters, are about 22 mm wide; stamens 5–7, anthers pale purple. Fruit, borne in loose few-fruited slightly compound long-pediceled clusters and ripening late in September, is oblong or usually obovate, full and rounded at the ends, 13–15 mm long, 12–14 mm thick, orange-scarlet, often mottled with orange at apex, capped by the erect fleshy bases of the lobes; flesh thick, sweet, orange; seed 3–4, thick and coarse, grooved on back, about 7 mm long.

Summerville, St. Clair County, Michigan, where very common. C. K. Dodge and W. W. Ashe, Sept., 1902; Oct., 1903; C. K. Dodge, May, 1903, Sept., 1903.

CRATAEGUS GRAVIS. A tree 6–7 m high with thorny scaly bark on the trunk, ascending fluted gray branches, and stout dull chestnut glabrous twigs, freely armed with stout 3–4 cm-long slightly recurved thorns. Leaves thick, firm, bright green, pubescent above when young, otherwise glabrous, ovate to nearly orbicular, 3–5 cm long, 2.5–5 cm wide, rounded or obtuse at base, finely and obtusely doubly serrate, several pairs of very shallow notches, turning dull yellow or brown

and falling in October. Flowers, appearing the last week in May in small loose slightly compound glabrous clusters, are about 20 mm wide; stamens 10, seldom 5–10, anthers rose-purple. Fruit, borne in small nearly simple clusters on rather long spreading pedicels and ripening in October, is slightly oblong, 8–10 mm long and 7–9 mm thick, flattened at the ends, dark red or crimson, seldom with orange spots at apex, capped by the closely sessile appressed lanceolate entire lobes, which are often appressed pubescent above; flesh firm, sweet, juicy, pale yellow; seed 4–5, small, 5–6 mm long, sometimes grooved on the back.

Port Huron, Michigan: common. W. W. Ashe and C. K. Dodge, September, 1902, October, 1903; C. K. Dodge, May and September, 1902, and 1903.

CRATAEGUS SEQUAX. Arborescent, 4 m in height, with a round crown of ascending flexuous branches; the purplish-brown usually glabrous twigs armed with many 1–5 cm-long rather stout thorns. Leaves soon nearly or quite glabrous, firm, deltoid, broadly ovate or ovate, 3–6 cm long, 2.7–5.5 cm wide, rounded or truncate at the base, usually 3–4 short acute lobes, sharply serrate, petiole slender, rarely puberulent. Flowers, appearing the second week in May in small compact slightly compound cymes, are about 20 mm wide; stamens 5–10, frequently 8, anthers purple. Fruit, ripening the last of September and falling with and after the leaves and borne in short compact usually simple clusters, is globose or subglobose 12–15 mm long and thick, dark red or crimson, often blotched with green or russet at the apex, the narrow subentire lobes spreading, reflexed or ascending.

C. L. Gruber and W. W. Ashe, Berks county, Pa.

CRATAEGUS VITTATA. Arborescent, 4–5 m high, with rather stout red-brown glabrous twigs sparingly armed with 5–6 cm-long stout thorns. Leaves ample, thin, firm, soon glabrous, broadly oval, the blades 5–7 cm long, 5–6 cm wide, rounded or truncate at the broad base, abruptly acute at apex, 3–4 pairs of broad short lobes; petioles very slender, 2.5–4

cm long. Flowers, appearing the first week in May in glabrous simple or compound compact corymbs, are from 15–20 mm wide; stamens 5–10, usually 8–10; anthers bright red-purple. Fruit, ripening early in September and gradually falling before the leaves, borne in simple few-fruited clusters on slender 1–2 cm-long pedicels, is subglobose or short cylindrous, 14–18 mm thick and long, red scarlet blotched with olive or russet, sparingly glaucous, capped with the narrow glabrous entire or serrulate spreading or erect lobes; flesh soft, thick, edible, acid, orange, often tinged with pink; seed 3–4, 6–8 mm long, deeply grooved on the back.

Pennsylvania, Berks county, frequent. W. W. Ashe and C. L. Gruber, Sept., 1902, and Sept., 1903; C. L. Gruber May and Sept., 1902, and May, June and Sept., 1903.

CRATAEGUS MINIATA. A shrub 2–3 m in height with ascending branches, with dark brown glabrous slender twigs armed with 3–4-cm long slender thorns. Leaves thin, glabrous, dark green, oval or broadly oval, 4–6 cm long, 3–5 cm wide, rounded at the usually broad base, abruptly acuminate at apex, 4–6 pairs of very short lobes beginning near the base. Flowers, appearing about the middle of May in glabrous compound rather small corymbs, are about 15 mm wide; stamens 5–10, usually 8; anthers pink. Fruit, borne in small compact usually compound clusters, ripening early in September and falling with the leaves, is oblong, 12–14 mm long, 9–13 mm thick, scarlet, sometimes spotted with olive or russet at the apex, glossy, capped with the small glabrous narrow entire reflexed or spreading lobes, or lobes deciduous; flesh yellow or pinkish; seed 2–3, 6–7 mm long, grooved on the back.

Pennsylvania, Berks county. C. L. Gruber and W. W. Ashe.

CRATAEGUS RUFIPES. A shrub about 2 m in height with glossy slender purplish-red glabrous nearly straight twigs, armed with numerous 2–4 cm-long thorns. Leaves thin but firm, bright green, lucid, when young silky, pubescent above, but at length glabrous, the blades ovate to oblong ovate, 5–7

cm long, 4–6 cm wide, rounded, rarely truncate or acute at base, acuminate at apex, 4–7 short very acute lobes beginning near the broad base; petiole stout, usually margined and glandular, purplish, as is the midrib. Flowers, appearing about the middle of May in many 6–20-flowered compound or simple glabrous corymbs are about 15 mm wide; stamens 5–8, anthers dark rose. Fruit, borne in small simple or compound clusters, ripening about the middle of September, is oblong, 12–14 mm long, 9–11 mm thick, scarlet frequently mottled with green or russet at the apex; the linear subentire nearly glabrous lobes reflexed; flesh soft, orange or reddish; seed 2–3, 6–7 mm long, 2–4 shallow grooves on back.

Pennsylvania, Berks county. C. L. Gruber and W. W. Ashe, Sept., 1903, C. L. Gruber, May and July, 1903.

CRATAEGUS MULTIFIDA. A shrub 1–2 m in height, with slender slightly zigzag red-brown glabrous twigs, sparingly armed with 4–7 cm-long thorns. The leaves are thin, firm, bright green, soon glabrous, broadly ovate in outline, the blades 4–5.5 cm wide, acuminate at apex, round or cordate, seldom obtuse at the broad base, 3–5 pairs of deep acuminate lobes, the lower pair spreading and with reflexed tips, sharply serrate or doubly serrate. Flowers, appearing the last week in May in rather small compact slightly compound glabrous corymbs, are about 15 mm wide; stamens usually 10. Fruit, borne in small compact compound drooping clusters, ripening late in September and falling with and after the leaves, is oblong, 11–14 mm long, 9–11 mm thick, rounded at the ends, crimson, capped by the closely sessile appressed, narrowly triangular usually entire lobes; flesh yellow, soft and pulpy, seed 4–5 mm, 6–7 mm long.

Sandy soil near the St. Clair River, Port Huron, Mich.

W. W. Ashe, and C. K. Dodge, September 1902; C. K. Dodge May 1902, May and September 1903.

CRATAEGUS TENERA. Arborescent in habit, about 3 m high, with rather short spreading branches; twigs red-brown, freely armed with short rather stout 2–3 cm-long ascending thorns.

Leaves glabrous, thin, ovate or broadly ovate, the blades 3–5 cm long, rounded or truncate at the broad serrate base, 3–4 pairs of short acute lobes, finely and sharply serrate. Inflorescence a many-flowered very compound glabrous drooping corymb; stamens small, usually 5–8. Fruit, borne in large compact compound drooping clusters, is oblong, 11–13 mm long, 9–10 mm thick, bright scarlet, sparingly pruinose, ripens about the the first of October and at once falls; lobes very long and narrow, usually entire, spreading, or are with deciduous tips and keeled base; flesh thick, pale yellow, white or pink, at length soft and pulpy, seed 3, rounded on the slightly grooved back, small, 5–6 mm long.

Sandusky, Ohio; E. Mosely and W. W. Ashe.

CRATAEGUS MARCIDA. Arborescent, 3–4 m high, with horizontal branches, and red-brown glabrous sparingly armed twigs. Leaves thick, firm, dark green and lucid above, glabrous, ovate, narrowed to the acute point from the broad rounded base, few shallow lobes, sharply doubly serrate, 4–6 cm long, the lower pairs of thin veins, arched. Inflorescence a large compound many-flowered glabrous corymb; stamens 10. Fruit, borne in large loose compound drooping corymbs, is depressed globose, 13-15 mm thick, 11-12 mm long, dark crimson with green apex, glaucous, lobes sub-entire, spreading from a broad base; flesh deep orange, firm and juicy; seed usually 4, shallow groved on the back.

Ohio: Leverettsburg, W. W. Ashe; Sandusky, E Mosely and W. W. Ashe; Garrettsville, R. J. Webb and W. W. Ashe. This beautiful thorn will probably prove to be common throughout Northern Ohio.

CRATAEGUS PROPINQUA. Arborescent in habit, 2-3 m high, branches slender, spreading, twigs slender, glabrous, red-brown, armed with slender 3-4 cm-long thorns. Leaves glabrous, thin but firm, light green, broadly ovate or rhombic, rounded or cuneate at the subentire base, the blades 3-5 cm long, very few shallow ascending lobes and deeply impressed straight ascending primary veins, sharply doubly serrate.

Inflorescence a 5-10-flowered slightly compound glabrous corymb; stamens 10. Fruit, borne in simple few-fruited clusters, is globose, 12-13 mm thick, green, russet and dull red, capped by the narrowly triangular, ascending, dry, subentire lobes; flesh pale yellow, firm; seed usually 3, 7-8 mm long, with shallow furrows on the broad rounded back.

Hillsides, Milan, Ohio. While this plant has characters which ally it to the Pruinosae, as is the case also with the preceding, it is probably best placed with the Tenuifoliae.

PRUINOSAE.

CRATAEGUS INGRATA. A bushy tree, 3-5 m in height, with red-brown twigs, occasionally slightly pubescent the first spring, but glabrous by fall, armed with numerous short 2-4 cm-long stout thorns. Leaves thin, pale green, pubescent below, especially on the viens, when young, ovate or broadly ovate, the blades 5-9 cm long, lobed above the middle with few very short teeth, rounded at the base, sharply serrate, petiole slender, pubescent, 3-4 cm long. Flowers, appearing about May 18th, in nearly simple 5-10-flowered, pubescent corymbs, are about 18 mm wide; stamens 20, anthers white. Fruit, borne in simple clusters on slender 2-3 cm-long pedicels, is subglobose, 12-14 mm thick, dull red; tube slightly projecting, the narrow lobes reflexed or deciduous: seed 3-5, the large ones ridged on the back, 7-8 mm long, narrowed at the base.

Near Pittsburg, Pennsylvania. J. A. Shafer, May 18, and October 26, 1902. J. A. Shafer and W. W. Ashe, September, 1901.

CRATAEGUS SITIENS. A stoloniferous shrub, seldom arborescent, forming thickets 2-4 m in height with thorny nearly black scaly bark and very slender brown-purple geniculate twigs, fully armed with slender 3-4 cm-long thorns. Leaves glabrous, thin, broadly ovate, truncate or rounded at the very broad base, 3-5 cm long and wide, with many pairs of deep lobes above the base, coarsely serrate. Petioles slender, 2-3

cm long. The flowers, appearing about May 20th in simple glabrous, 3-5-flowered cymes, are about 24 mm wide; stamens 20, anthers purple. The fruit, solitary or in few-fruited clusters on strict slender 1.5 to 2 cm-long pedicels, is obovate, 12-14 mm thick, green mottled with russet; cavity very broad, the short broad entire lobes reflexed; the tube long projecting or often deciduous; flesh hard and green, seed 4-5, small, 6 mm long, lateral faces broad and flat.

St. Clair County, Michigan. Not common. W. W. Ashe and C. K. Dodge, Oct., 1902; C. K. Dodge May 23, 1903, Oct., 1903.

BOYNTONIANAE.

CRATAEGUS RESES. A many-stemmed shrub, forming thickets about 2 m high, the rather stout chesnut twigs glabrous, and like the stems almost unarmed. Leaves glabrous, thick, soft, very dark green above, very pale beneath, the blades elliptic or ovate or oblong ovate, 6-9 cm long, 4-6 cm wide, gradually narrowed from near the middle to the narrow rounded base, crenate, 2-3 pairs of short broad obtuse notches above the middle, turning red bronze or yellow and falling late in autumn; petiole short and stout, winged above. Flowers appear about the middle of May in simple long-pedicelled glabrous 5-10-flowered cymes; stamens 10; anthers cream. Fruit ripening in October and falling largely after the leaves, borne in 1-5 fruited clusters, on long stout, often strict pedicels, is subglobose, usually slightly narrowed at the base, 13-16 mm thick, dark red mottled with russet or green, dull and glaucous, or glossy, capped by the oblong, coarsely glandular serrate glabrous lobes borne on the projecting tube, or often lobes deciduous; flesh firm, orange or reddish, bitter; seed usually 4-5, 7-8 mm long, shallow 1-3 grooved on the back.

Pennsylvania, Berks County: C. L. Gruber and W. W. Ashe, Sept., 1903; C. L. Gruber, May, 1903.

AMARAE.

CRATAEGUS OLIDA. A flat bushy tree 5 m in height, with glabrous bright purple-brown twigs armed with numerous slender 4-5 cm-long darker thorns. Leaves glabrous, thick and firm, the blades 4-6 cm long, ovate, obovate or nearly orbicular, 2-3 pairs of shallow lobes above the middle, obtusely serrate nearly to the base; petiole stout, 1.5-2 cm long, broadly margined and glandular. The flowers are borne in 5-12 flowered glabrous compound strict corymbs; stamens normally 10, filaments stout, 5-6 mm long, lobes narrowly triangular, subentire, reflexed after anthesis. Fruit, falling after the leaves, and borne in slightly compound clusters, is obovate or pyriform, 15-19 mm long, 14-16 mm thick, golden yellow; flesh yellow, firm, slightly bitter; seed 2-4, usually 3, 7-8 mm long, thick and coarse, the broad back grooved.

J. A. Shafer, May 30 and Nov. 9, 1902; Pyler Falls, Pennsylvania.

INACTIVE THORIUM.*

FRITZ ZERBAN, PH.D., (CARNEGIE RESEARCH ASSISTANT).

It was soon after the discovery of the well-known X-rays by Roentgen, that Becquerel, in Paris, observed that remarkable property of Uranium potassium sulphate by which it affected the photographic plate through light-tight black paper, when the sun shone on the salt. At first he thought that this action was brought about by the fluorescence of the Uranium salt, but very soon discovered that nonfluorescent Uranium compounds and the metal itself effected the same action, and that the concurrence of the sun's rays was not necessary, the aforementioned phenomenon appearing also in a thoroughly dark room. He called this peculiar property of the Uranium "radioactivity", and for the rays, which produce the blackening of the photographic plate, the name of "Becquerel rays" was adopted. It was shown then that the Uranium compounds had still another remarkable property, namely of diminishing the conductivity of the air for electricity, so that a charged electroscope loses its charge more rapidly than usual, if a Uranium compound is brought near it. Thirdly, the Becquerel rays excite, like the X-rays, the fluorescence of a Barium platinocyanide screen.

Three methods for testing the radioactivity of bodies were thus acquired and different investigators discovered, besides the Uranium, some other radioactive substances. Mr. and Mrs. Curie found in Pitchblende two such bodies; Polonium, which is similar to Bismuth, and Radium, which soon brought to its discoverers great fame all over the world. The Radium occurs with Barium, and is separated from it by very laborious and protracted operations. As Radium is the most strongly

* Read before the North Carolina Academy of Science, Wake Forest Meeting, May 14th, 1904.

radioactive body, one can show with its salts in the best manner the action of the Becquerel rays.

According to the investigations of Rutherford and his collaborators, the different actions of the radioactive bodies are not caused by one kind of rays, but by different ones. The rays which cause the discharge of the electroscope he called α-rays. They are easily absorbed by different substances and only slightly deflected by a magnet.

The β-rays on the other hand produce chiefly the photographic action, even penetrating thin metal sheets, wood, and so on, and are deviated easily in a magnetic field. Rutherford found also a third kind of rays, the γ-rays, the source of which is not clearly defined. Perhaps these, according to the suggestion of Dr. Baskerville, are derived from the β-rays, as the Roentgen rays arise from the cathode rays. A discussion of this matter need not hold our attention today however.

It is noteworthy indeed, that the radioactive substances emit not only *rays*, but *material particles* too, in form of a gas. It may be swept along by a stream of air blown over the substance and follows its course, unlike the light rays. It also diminishes the conductivity of the air. As a real gas it has been condensed to a liquid boiling at about 135° below zero. Rutherford called this very interesting property of the radioactive bodies "emanation".

Rutherford performed his preliminary experiments not with Radium, Uranium or Polonium, but with another radioactive substance, Thorium. Mrs. Curie and G. C. Schmidt had found, independently of each other, that the Thorium compounds are also radioactive. Some time later Debierne discovered in Pitchblende a body similar to Thorium. It gave all the reactions of real Thoria: precipitation by Ammonia, Alkali, Ammonium sulphide, also by oxalic acid, strong acids being present, and in neutral solution by Sodium thiosulphate and Hydrogen dioxide. Its hydroxide was insoluble in hydrofluoric acid and Potassium fluoride. But differing from the ordinary Thorium it was extremely and permanently active.

Debierne assumed it to be a new element and gave it the name "Actinium".

Now the question was raised, whether the radioactivity of the Thorium compounds was caused by admixture of a little quantity of Actinium, and whether Thorium obtained by any means whatever is in every case radioactive.

Rutherford tried to answer the question, whence the activity of the Thoria came. He, by precipitation of Thoria with ammonia, obtained a filtrate which was much more radioactive than the precipitate. He said that the activity of Thorium is due to the body contained in the liquid and called it Th X. Subsequent investigations from this savant indicate the continued regeneration of Th X. In the laboratory of the University of North Carolina we have experiments planned which promise an explanation of this, so we may defer further consideration for the present.

Professor Hofmann, in Munich, and I, attacked the problem and the results of our investigations are briefly presented here. Incidentally it must be noticed that the Thorium, of which I am talking, means the old Thorium, the elementary nature of which is now getting very precarious by the splendid investigations of Dr. Baskerville which are astonishing all the world.

To decide the questions mentioned above it was at first necessary to study the minerals, from which the Thorium preparations to be examined were obtained. All the preceding investigations were made with commercial Thorium compounds which came from monazite sand, exclusively I think. We examined the Thorium obtained from the following minerals: bröggerite, cleveite, euxenite, samarskite, fergusonite, xenotine, thorite, orangite, aschynite, monazite sand, gadolinite, orthite and yttrotitanite. The Thoria was extracted from these minerals by different methods according to their composition. It was always separated from the other rare earths by dissolving its oxalate in a hot solution of ammonium oxalate and precipitating the Thoria in the cooled and diluted filtrate by hydrochloric acid.

In this manner we obtained from the four first mentioned minerals, bröggerite, cleveite, euxenite and samarskite, some strong and some very strong active Thorium preparations, far surpassing the activity of the usual Thorium compounds. The assumption of the presence of Actinium therein was tenable, so we tried then, like Mr. and Mrs. Curie with Radium, to separate the Actinium by means of fractionation. And to all appearance we succeeded in this way, for we could accumulate the activity in one part of the fractions. It happened by fractional precipitation with Potassium sulphate, Sodium thiosulphate, Potassium chromate, Hydrogen dioxide, and fractional solution in Ammonium carbonate.

Our work was suspended during the vacation in 1901. On resumption of the investigations our previously very strongly active preparations had lost nearly all their activity upon the photographic plate and the electroscope. Thus it was shown that the Thorium could not possibly contain a primarily active body. For these, as for instance Radium and Actinium, behave quite differently. Immediately after their separation they show a certain quantity of radioactivity, which increases within a few weeks to a maximum, and then remains *constant* during several years, at least according to our measuring methods. But Thorium behaved quite differently. Its activity rather diminished, and then indeed it reserved constantly a very little activity. The β-, or photographic action fell down to an insignificant amount, whereas the α-radiation assumed about the value of the weak Uranium radiation.

As therefore Thorium evidently is not a primarily radioactive body, the further question was to be decided: where does the activity of the Thorium compounds come from? The investigation of the other minerals gave us the key to this problem. The four first mentioned minerals contain a great deal of Uranium in comparison with the amount of Thorium present. We found furthermore: the more Uranium and the less Thorium a mineral contains, the more active is the Thorium obtained from it.

It was quite important to secure Thoria from several minerals containing *no* Uranium, as from Norwegian gadolinite, orthite and yttrotitanite. Thorium separated from these minerals is inactive upon the plate and the electroscope. Mr. Curie was kind enough to make a control determination of the activity of one of these preparations, and he also found it practically inactive or if possessing any activity at all, its value is only one seventh of the activity ever observed.

The inactive Thorium shows all chemical properties of ordinary Thorium. To prove that it was really Thorium I made an approximate determination of its atomic weight, and found 222.7. This figure is of value mainly, as it indicates an element with an atomic weight above 200.

It is most probable that the Thorium itself does not possess any primary activity at all, but that it receives its activity from other primarily active bodies like Uranium or Radium, or even from the *air*, which, according to the investigations of Elster and Geitel contains *always* and *everywhere*, more or less radioactive particles. We succeeded in securing a further very important proof of our opinion, by producing artificially active Thorium from an inactive one, and by showing that this artificially active Thorium behaves in every way like the natural active Thorium.

The experiments were made as follows: to a solution of inactive Thorium nitrate a ten to twenty-fold excess of Uranium nitrate in solution was added; the mixture was then kept about two weeks, and the thoria precipitated with oxalic acid. The well washed and burned Thorium preparation behaved then exactly like the thoria of bröggerite and cleveite. It showed a very considerable amount of α- and β-activity. But after a year the β-radiation disappeared nearly altogether, and the α-radiation recovered gradually a small, but finally constant value. In a similar way as with Uranium, we rendered thoria active by means of Polonium.

Although *per se* inactive Thorim can be obtained of some minerals, and although, on the other hand, the at first

strongly active Thorium loses the largest part of its activity within a few months, we have not yet secured Thorium entirely free from the last remnant of activity. In company with Dr. Baskerville I made some experiments about this, using the property of Barium and Lead to take with them the activity, when precipitated in a mixture with an active salt by means of sulphuric acid or Hydrogen sulphide. In these experiments we did not use the original Thorium, but its three components, about which Dr. Baskerville will speak to you in a few moments. We dissolved a little quantity each of Berzelium, Thorium and Carolinium salt, one of which must surely be the bearer of the original Thorium activity, added a large excess of Barium chloride, kept the whole during three days and then precipitated the Barium with sulphuric acid. The Berzelium, Thorium and Carolinium obtained from the filtrate were then nearly inactive, but within two weeks they regained their original activity. Nor did we succeed in removing the activity from the original Thorium by adding a large excess of Lead salt and precipitating the latter with Hydrogen sulphide.

While one may secure inactive Thorium direct from certain minerals, it has been quite impossible so far to remove the last remnant of activity from Thorium that has once been active.

As in the meantime Dr. Baskerville happened to divide the old Thorium into three constituents, it is very interesting indeed to investigate what part the three new elements take in the radioactivity of the old Thorium. So far it has been found that all three, although not in the same degree, are active. But possibly the new elements are not yet pure enough; hence we hope by further methods of purification to reach that point, so that we can give with the description of all their properties also this of the degree of their activity.

In the list of members of the North Carolina Academy of Science, published in the last issue of this journal, the following names were omitted:

Stevens, F. L.,	West Raleigh.
Stevens, Mrs. F. L.,	West Raleigh.
Venable, Francis P.,	Chapel Hill.
Wilson, H. V.,	Chapel Hill.
Wilson, R. N.,	Guilford College.
Winston, Geo. T.,	West Raleigh.
Williams, C. B.,	Raleigh.
Wheeler, A. S.,	Chapel Hill.